

Aging of rubbers in oils

26883
S/081/61/000/013/023/028
B117/B203

between 60 and 80°C, and 9 kcal/mole in oil at >80°C. This reduction is due to the effect of oil on rubber oxidation at high temperatures. [-17 kcal/mole for the aging of stretched rubber in oil. [Abstracter's note: Complete translation.]]

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B117/B203

15.9300

AUTHORS: Degteva, T. G., Nosov, Yu. A., Lazarenko, Ya. F., Fedorova,
V. G., Kuz'minskiy, A. S.

TITLE: Aging of rubber packings in oil

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 13, 1961, 653, abstract
1311331 (Tr. N.-i. in-ta rezin, prom-sti, sb. 6, 1960, 69-83)

TEXT: The authors developed a quick method of estimating the service life of CKH-18 (SKN-18) packing rings in oil at $\sim 20^{\circ}\text{C}$. Tests were made in special imitators simulating the packings of machines. Rubber rings originally compressed to 10-30% aged between 60 and 80°C . Deformation and radial compression were periodically measured. A contact pressure of 2.5 kg/cm^2 is sufficient to make the packing completely tight at 20°C . In this connection, $\sim 100\%$ of the permanent elongation (ξ) is accumulated, and the stress nearly vanishes. After finding the kinetic curves for the accumulation of ξ , the authors determined the apparent activation energy

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of aging and the service life of packings in joints at 25°C, the latter being about 10 years (considering the correction factor). The service life was practically calculated for 80%. For packings operating at -60°C, the critical value of the contact pressure required for a perfect seal rose from 7.5 up to 13 kg/cm². Leakiness is related with the loss in elastic properties of the rubber. [Abstracter's note: Complete translation.]

Card 2/2

KUZ'MINSKIY, A.S., doktor khimicheskikh nauk; FEL'DSHTEYN, L.S.;
REYTLINGER, S.A., kand.tekhn.nauk

Surface crystallization of the ingredients of rubber mixtures.
Trudy NIIRP no. 6:84-91 '60. (MIRA 13:12)
(Rubber)

26880

S/081/61/000/013/020/028
B117/B203

15.9300

AUTHORS: Angert, L. G., Zenchenko, A. I., Kuz'minskiy, A. S.

TITLE: Volatilization of ingredients from rubbers

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 13, 1961, 652, abstract
1311328 (Tr. N.-i. in-ta rezin. prom-sti, sb. 6, 1960, 92-101)

TEXT: The authors studied the kinetics of volatilization of Neozone D in N_2 flow from СКБ(СКБ) plates with a standard surface and given thickness (h). The kinetic curves were described with an equation of the type $C/C_0 = [1 - \exp(-kt)]$ (I), where C is the amount of ingredient volatilized at the instant t, in % by weight of rubber; C_0 the initial amount of the ingredient; and K the rate constant of volatilization. The activation energy (E) of the process is 14 kcal/mole. The equation $K = K_0 [\exp(-E/RT)] [(w_t/(b + w_t))] (1 + aC_0)/h$ (II) was derived on the basis of the found dependences of K on temperature (T), flow velocity of the gas (w_t), C_0 , and h. K_0 is a constant depending on the nature of the

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substance studied and of the polymer. a and b are experimentally found. The loss of ingredient can be calculated from (I) and (II) for various polymers and test conditions. The volatilization rate decreases in the order of polymers: polyethylene>fluorine rubber>polybutadiene rubber>CKC-30 (SKS-30)>CKH-26 (SKN-26)>nairit (this agrees with data on the change in solubility); volatilization of SKB is slowed down by introduction of filler, more by channel black than by chalk. In radiation vulcanizates of SKB, volatilization is slowed down by an increase in density of the lattice. [Abstracter's note: Complete translation.]

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KUZ'MINSKIY, A.S., doktor khim.nauk; BORKOVA, L.V.

Evolution of hydrogen sulfide during the vulcanization of
ebonite. Trudy NIIRP no. 7:67-73 '60. (MIRA 14:1)
(Rubber) (Hydrogen sulfide)

85656

15.9300 1451,2209,2109

S/138/60/000/009/003/012
A051/A029

AUTHORS: Angert, L.G.; Kuz'minskiy, A.S.

TITLE: Aging of Rubbers Vulcanized with Thiuramdisulfides

PERIODICAL: Kauchuk i Rezina, 1960, No. 9, pp. 15 - 20

TEXT: The aging regularities of thiuramdisulfide-vulcanized rubbers (i.e., thiuram rubbers) and the causes of their heat resistance were studied. The CKB (SKB) polybutadiene polymer was used as the object of investigation, as well as its non-filled and partially-filled vulcanizates. The aging process of the materials was characterized by the oxidation kinetics, which, in turn, was determined on a "micro-oxidation apparatus" (Ref. 5). The stability index was determined by the oxidation rate in an induction period and by the duration of this period. The change in structure of the vulcanizate during the aging process was determined by the magnitude of the static modulus, i.e., the vulcanizate modulus determined after 3 hours of relaxation of tension in the sample at a constant load. The temperature range of the investigation was between 130 - 150°C. The effect of the presence of zinc oxide in the rubber mixture on the heat-resistance of the vulcanizates was determined. A high heat-resistance was obtained in the presence

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of zinc dithiocarbamates, which are effective inhibitors of the oxidation process. They are formed by a reaction between the zinc oxide and the dithiocarbamic acid. In the oxidation of the I vulcanizate, from which all free ingredients were extracted, the induction period was absent, an autocatalytic process began at the start, and the sample rapidly deteriorated, since in this case the pure polymer was subjected to oxidation, encased primarily by transverse bonds of the C-S-C type. Thus, the effects of the individual free components on the oxidation process of vulcanizate I were investigated, and it was noted that zinc oxide hardly affects the oxidation process, thiuram has only a slight effect and zinc diethyl-dithiocarbamate is a strong inhibitor, especially at a temperature of 130°C. However, the latter does not inhibit the process of thermal change of the rubber when oxygen is absent. In investigating the reaction mechanism of the dithiocarbamates as oxidation inhibitors it was found that during the inhibition process part of the zinc dithiocarbamate gradually reacts with the molecules of the polymer, as a result of the interaction of the dithiocarbamate with the ROO^\cdot , RO^\cdot or R^\cdot radicals, or with the intermediate, non-stable products, such as $ROOH$, $RCHO$, forming during the oxidation of the polymer. The data obtained revealed that dithiocarbamate could not act as an inhibitor of the thermal change in the polymer, and therefore, does not react with hydrocarbon radical (R^\cdot). Its action

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Aging of Rubbers Vulcanized with Thiuramidisulfides

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should be directed at oxygen-containing active centers of the polymer being oxidized. In studying the effect of the mutual action of dithiocarbamate and phenyl- β -naphthylamine on the rubber aging process it was seen that the addition of phenyl- β -naphthylamine to a nonfilled thiuram vulcanizate (containing dithiocarbamate) is rather effective. However, the effect of phenyl- β -naphthylamine in filled thiuram rubbers depends on the rubber contained in it. Phenyl- β -naphthylamine and dithiocarbamate taken together are most effective as inhibitors. The most effective salts of dithiocarbamic acid as oxidation inhibitors proved to be the ethyl and butyl derivatives of zinc, copper and bismuth dithiocarbamates. These compounds should be used in combination with antioxidants of the amino-class in order to increase the aging resistance of a number of other types of rubbers. There are 8 figures and 18 references: 9 Soviet, 8 English, 1 German. ✓

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti (Scientific-Research Institute of the Rubber Industry).

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S/13860/000/011/004/010
A051/A029

AUTHORS: Kuz'minskiy, A.S., Frenkel', R.Sh.

TITLE: Investigating the Effects of Scorching on the Properties
of Rubber

PERIODICAL: Kauchuk i rezina, 1960, No. 11, pp. 18-20

TEXT: The authors point out the formation of transverse bonds in the case of scorching, leading to a wide range of changes in the vulcanization lattice density. Attention is drawn to the fact that in addition to the transverse bonds being broken when rubber is processed on rollers, destruction and a branching of the molecular chains can also occur which in turn affect the physical and mechanical properties of rubbers. The authors have attempted to estimate the degree to which scorching of mixtures can be permitted without causing a significant drop in the mechanical properties of the vulcanizates. A study was also made of the effect of the nature of the destroyed mono- or polysulfide bonds, on the technological properties of the mixtures and on the mechanical indices of rubbers. Vulcanizates of non-filled mixtures based on natural rubber without sulfur and with thiuram

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Investigating the Effects of Scorching on the Properties of Rubber

and vulcanizates with sulfur containing $\Delta\Phi\Gamma$ (DFG) were chosen as the objects to be investigated. The vulcanization of the mixtures was carried out for various periods of time in order to produce vulcanizates differing in their density of the spatial lattice and the vulcanizates obtained were processed on cold rollers. The density of the transverse bonds was determined by the method of the equilibrium coefficient. Figs. 1-3 show the change in the plasticity according to Carriere, of vulcanizates with different thickness of the lattice, when processed on the rollers. It was seen that vulcanizates containing monosulfide and polysulfide bonds with an equilibrium coefficient of 3-4 kg/cm² rapidly deteriorate on the rollers and immediately form a stable skin. Vulcanizates with higher values of the equilibrium coefficients were also found to pass into the plastic state. It was noted that the greater is the density of the space lattice, the longer the duration of the rolling process whereby the vulcanizates with monosulfide bonds passed into the plastic state more rapidly than those with polysulfide bonds. Tables 1 and 2 list the physico-mechanical properties and aging resistance of rubbers obtained from reclaimed

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vulcanizates having various bond types. From these data it is seen that with an increase in the lattice thickness in vulcanizates with the mono- or polysulfide bonds the physico-mechanical properties of the rubbers produced from these vulcanizates decrease. The following conclusions are drawn: 1) When vulcanizates containing transverse bonds are processed on rollers they are converted to the plastic state. 2) Vulcanizates with an equilibrium coefficient not over 3-4 kg/cm² rapidly deteriorate on the rollers and immediately form a stable skin. With an increase in the thickness of the lattice of the vulcanizates, a lengthy processing time is required in order to convert these to the plastic state. 3) Vulcanizates with monosulfide bonds pass more rapidly into the plastic state than those with polysulfide bonds. 4) With an increase in the thickness of the vulcanizates with mono- and polysulfide bonds the physico-mechanical properties drop in rubbers obtained from these vulcanizates. The aging resistance of the vulcanizates obtained from monosulfide bond material does not change with an increase in the thickness of the lattice and in rubbers prepared from vulcanizates with polysulfide bonds it sharply falls.

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Investigating the Effects of Squeezing on the Properties of Rubber

There are 2 tables, 3 graphs and 2 Soviet references.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti
(Scientific Research Institute of the Rubber Industry)

Fig. 1:

Vertical legend:

Plasticity according to Carriere

Horizontal legend:

rolling duration, min.

Change in the plasticity of the
vulcanizates with monosulfide
bonds in rolling.

1-vulcanizate with an initial
equilibrium coefficient of 1.7 kg/cm²
2-20 kg/cm², 3-3.0 kg/cm²
4-6.0 kg/cm², 5-11.0 kg/cm²



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Investigating the Effects of Scorching on the Properties of Rubber

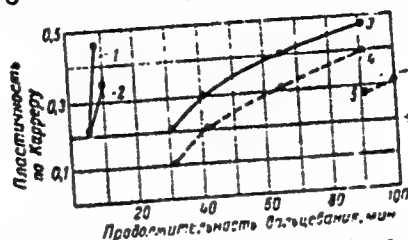
Fig. 2:

Vertical legend:

Plasticity according to Carriere

Horizontal legend:

rolling duration, min.



Change in the plasticity of the vulcanizates with polysulfide bonds in rolling: 1-vulcanizate with initial equilibrium coefficient of 1.7 kg/cm², 2-3.0 kg/cm², 3-6.0 kg/cm², 4-11.0 kg/cm², 5-18.8 kg/cm².

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Investigating the Effect of Scorching on the Properties of Rubber

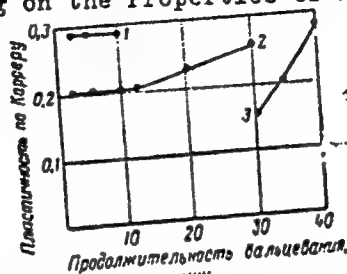
Fig. 3:

Vertical legend:

Plasticity according to Carriere

Horizontal legend:

rolling duration, min.



Plasticity change in vulcanizates with carbon bonds during rolling:
1-vulcanizates with initial equilibrium coefficient of 1.7 kg/cm²
2-3.0 kg/cm², 3-4.0 kg/cm²

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Investigating the Effect of Scorching on the Properties of Rubber

Table 1: Physico-mechanical properties and aging resistance of rubbers produced from vulcanizates containing monosulfide bonds

① Тип смеси	② Продолжительность вулканизации при 4 атм., мин.	③ Сопротивление разрыву, кг/см²	④ Относительное удлинение, %	⑤ Остаточное удлинение, %	⑥ Модуль при 500% удлинении, кг/см²	⑦ Равновесный модуль, кг/см²	⑧ Коэффициент теплового старения при 100° через 24 часа	
							⑨ по сопротивлению разрыву	⑩ по относительному удлинению
⑬ Исходная	15	228	800	4	50	11,3	0.95	0.93
⑭ Из вулканизата с равновесным модулем 1,7 кг/см², вальцованного 7 мин.	9	157	700	6	55	10,1	0.94	0.87
⑮ Из вулканизата с равновесным модулем 3,0 кг/см², вальцованного 7 мин.	15	150	700	6	50	9,0	0.82	0.85
⑯ Из вулканизата с равновесным модулем 6,0 кг/см², вальцованного 40 мин.	20	135	710	4	35	8,1	0.71	0.87
⑰ Из вулканизата с равновесным модулем 11 кг/см², вальцованного 40 мин.	25	120	735	5	23	6,8	0.67	0.90

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Investigating the Effect of Scorching on the Properties of Rubber

Table 1 (continued): ① mixture type; ② vulcanization duration at 4 atm, min; ③ tear-resistance, kg/cm²; ④ relative elongation, %; ⑤ residual elongation %; ⑥ coefficient at 500%, elongation, kg/cm²; ⑦ equilibrium coefficient, kg/cm²; ⑧ coefficient of thermal aging at 100°C, after 24 h; ⑨ according to tear-resistance; ⑩ according to relative elongation; ⑪ initial; ⑫ from vulcanizates with an equilibrium coefficient of 1.7 kg/cm², rolled for 7 min; ⑬ from vulcanizates with an equilibrium coefficient of 3.0 kg/cm², rolled for 7 min; ⑭ from vulcanizates with an equilibrium coefficient of 6.0 kg/cm², rolled for 40 min; ⑮ from vulcanizates with an equilibrium coefficient of 11 kg/cm², rolled for 40 min.

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Investigating the Effect of Scorching on the Properties of Rubber

Table 2: Physico-mechanical properties and aging resistance of rubbers produced from vulcanizates containing polysulfide bonds

① Тип смеси	② Прочность на разрыв, кг/см²	③ Прочность на разрыв, кг/см²	④ Относительное удлинение, %	⑤ Остаточное удлинение, %	⑥ Модуль при 200% удлинении, кг/см²	⑦ Равновесный модуль, кг/см²	⑧ Коэффициент теплового старения при 100° через 24 часа	
							по сопротивлению разрыву	по относительному удлинению
⑪ Исходная	15	265	770	12	30	18,8	0.66	0.85
⑫ Из вулканизата с равновесным модулем 1.7 кг/см², вальцованного 7 мин.	17	250	620	16	39	19,3	0.6	0.89
⑬ Из вулканизата с равновесным модулем 3.0 кг/см², вальцованного 10 мин.	14	195	590	12	31	14	0.5	0.8
⑭ Из вулканизата с равновесным модулем 6.0 кг/см², вальцованного 40 мин.	14	160	590	14	32	13	0.21	0.44
⑮ Из вулканизата с равновесным модулем 11 кг/см², вальцованного 40 мин.	8	155	580	20	34	12	0.13	0.34
Из вулканизата с равновесным модулем 18.8 кг/см², вальцованного 90 мин.	8	92	510	12	22	16	0.1	0.18

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Investigating the Effect of Scorching on the Properties of Rubber

Table 2 (continued): ① mixture type; ② vulcanization duration at 4 atm, min; ③ tear-resistance, kg/cm²; ④ relative elongation, %; ⑤ residual elongation %; ⑥ coefficient at 500% elongation, kg/cm²; ⑦ equilibrium coefficient, kg/cm²; ⑧ coefficient of thermal aging at 100°C, after 24 h; ⑨ according to tear-resistance; ⑩ according to relative elongation; ⑪ initial; ⑫ from vulcanizates with an equilibrium coefficient of 1.7 kg/cm², rolled for 7 min; ⑬ from vulcanizates with an equilibrium coefficient of 3.0 kg/cm², rolled for 10 min; ⑭ from vulcanizates with an equilibrium coefficient of 6.0 kg/cm², rolled for 40 min; ⑮ from vulcanizates with an equilibrium coefficient of 18.8 kg/cm², rolled for 90 min.

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86230

158000 also 1526

S/030/60/000/011/006/026
B021/B059

AUTHORS: Neyman, M. B., Doctor of Chemical Sciences
Kuz'minskiy, A. S., Doctor of Chemical Sciences
Angert, L. G., Candidate of Chemical Sciences

TITLE: Scientific Problems of Polymer Stabilization

PERIODICAL: Vestnik Akademii nauk SSSR, 1960, No. 11, pp. 36-50

TEXT: This paper on the present state and future trends of Soviet research in the field of polymer stabilization is dedicated in its first part to the problem of aging and stabilization of plastic masses, in its second part to the same problems for rubbers. Degradation of polymers under the action of heat, oxygen, light, and radioactive radiation is discussed. Under external affections linkage, formation of structure between the polymer molecules may occur. Degradation as well as structuration lead to unwanted changes of mechanical and electrical properties of polymeric materials. Oxidation inhibitors, photostabilizers, aging inhibitors and other ingredients must be added to polymers in order to guarantee their working and to satisfy technical requirements. Therefore, production of polymers and of various stabilizers must be developed in parallel. Since years K. I. Ivanov
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Scientific Problems of Polymer Stabilization

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and collaborators have been investigating the mechanism of oxidation inhibition of lubricants. Shortly ago it was shown in S. S. Medvedev's laboratory that formic acid and formates inhibit oxidizing of hydrocarbons and of some polymers. A. S. Danyushevskiy and collaborators investigated a large number of stabilizers for polyvinylchloride! A. A. Berlin investigated stabilization of polyvinylchloride with epoxy compounds. The mechanism of the oxidation of organic substances, among them also polymers, was explained by a theory of N. N. Semenov. At the Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR) it was shown short time ago, that during a mild oxidation of some oxidation inhibitors, stable radicals may form, which were discovered by means of the method of electron paramagnetic resonance (Fig. 1). The action of inhibitors is explained according to a theory by N. N. Semenov. Measurements of the induction period and its dependence on inhibitor concentration are mentioned. P. I. Levin and A. F. Lukovnikov investigated in the laboratory of the Institute of Chemical Physics a number of mixtures of mercaptane and sulfides with aromatic amines as inhibitors of thermal oxidation. It is possible to measure the diffusion coefficients of stabilizers with great accuracy by using the method of tagging with radioactive isotopes. This was shown by B. A. Gromov, V. B. Miller, and Yu. A. Shlyapnikov. The

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problem of finding appropriate inhibitor combinations for plastics should be solved not only by the Institutes of the Akademiya nauk SSSR (Academy of Sciences USSR) and the Academies of Sciences of the Republics of the Union, but also by the Institutes of the Gosudarstvennyy komitet Soveta Ministrov SSSR po khimii (State Committee of Chemistry of the Council of Ministers USSR) and the laboratories of the schools of higher learning. This paper deals only with a few problems of the manifold rubbers since many articles have been devoted to that task already. The chief reason for thermal aging of rubber at temperatures below 150°C is an oxidation of polymeric molecules with atmospheric oxygen. Secondary amines and phenols serve as oxidation inhibitors of rubber. The aging processes of rubbers are rendered complicated by various impurities. Aging of vulcanized rubbers is different in this respect from ordinary rubber, chiefly because of a number of various free and bound components. The Nauchnyy sovet po vysokomolekulyarnym soyedineniyam (Scientific Council for Highmolecular Compounds) at the Presidium of the Academy of Sciences USSR, together with the State Committee of Chemistry of the Council of Ministers USSR, on June 6, 1960, adopted a joint resolution concerning the development of scientific and industrial research on the stabilization of polymers. This resolution provides the organization of a new laboratory of the Academy of Sciences

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USSR in Gor'kiy for the synthesis of stabilizers for the purpose of finding new types of inhibitors. A number of laboratories and test plants for the same purpose is planned for Tambov. The Institute of Chemical Physics and its Noginskiy filial (Noginsk Branch) are expanding their research work on polymers. The following institutes of the Academy of Sciences USSR are intended to be charged with these investigations: Institut elementoorganicheskikh soyedineniy (Institute of Elemental-organic Compounds), Institut vysokomolekulyarnykh soyedineniy (Institute of Highmolecular Compounds), as well as the laboratories of the Moskovskiy universitet (Moscow University), Moskovskiy tekstil'nyy institut (Moscow Textile Institute), of the Kazanskiy khimiko-tekhnologicheskoy institut (Kazan' Institute of Chemical Technology), and of a number of schools of higher learning. The laboratories of the following institutes shall be enlarged and new ones for the stabilization of polymers are planned: Fiziko-khimicheskiy institut im. L. Ya. Karpeva (Physicochemical Institute imeni L. Ya. Karpov), Institut plasticheskikh mass (Plastics Institute), Institut polimerizatsionnykh plasticheskikh mass (Institute of Polymerized Plastics), Institut sinteticheskogo kauchuka (Institute of Synthetic Rubber), Institut rezincvoy promyshlennosti (Institute of the Rubber Industry), Institut shinnoy promyshlennosti (Institute of Tire Manufacturing), and Institut iskusstvennogo volokna

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(Institute of Synthetic Fiber). A commission with Academician V. A. Kargin in the chair is entrusted with the coordination of the studies on the stabilization of polymers and with the preparation of construction plans for test plants for the sovmarkhoz. In 1961, the Institute of Chemical Physics intends to convene a special conference for the purpose of generalizing work in the field of the degradation and stabilization of polymers. There are 4 figures and 20 references: 17 Soviet, 2 US, and 1 British. ✓

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KUZ'INSKIY, A.S.; BASS, S.I.

Summing up the results of the International Symposium on Macromolecular Chemistry in 1960. Kauch.i rez. 19 no.10:1-6 0 '60.
(MIRA 13:10)

(Macromolecular compounds—Congresses)

KUZ'MINSKIY, A.S.; FRENKEL', R.Sh.

Effect of premature vulcanization on the properties of rubber.
Kauch. i rez. 19 no. 11:18-20 N '60. (MIRA 13:11)

1. Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti.
(Vulcanization)

68699

S/069/60/022/01/001/025
D034/D003

54 15.9130

AUTHOR: Angert, L.G., Zenchenko, A.I., Kuz'minskiy, A.S.
TITLE: Volatilization of Ingredients from Polymers
PERIODICAL: Kolloidnyy zhurnal, 1960, Vol 'XXII, Nr 1, pp 2-8 (USSR)
ABSTRACT: The present study was carried out to establish the empiric rules characterizing the behaviour of ingredients in caoutchouc and rubber under various conditions, and also to consider the problem from the theoretical standpoint. Object of the study was the volatilization of an antioxidant, phenyl- β -naphthylamine, from a rubber plate, while heating the latter in a gas current. The investigation method was as follows: Sodium butadiene rubber (SKB, without antioxidant) was mixed on micro-rollers with phenyl- β -naphthylamine. From the mixture obtained, plates of a given thickness were pressed. The volatilization of the antioxidant from a caoutchouc plate with

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Volatilization of Ingredients from Polymers

standard surface (150 x 10 mm) was carried out in a glass tube 18 mm in diameter, the caoutchouc sample being placed on a glass support. The tube was laid into a horizontal tube furnace heated with a silicone liquid which was forced in from a Vobser (sic) thermostat (see diagram). The nitrogen current passing through the tube carried the vapors of the antioxidant from the heated tube section into an attached trap immersed into a cooling mixture. The antioxidant condensing in the trap was quantitatively determined with the colorimetric method. The volatilization process was studied at temperatures above 100 C. The rate of volatilization of the antioxidant was determined with respect to the velocity of the nitrogen current passing over the plate, to the plate thickness and to the initial concentration of the ingredient. The activation energy of the volatilization process is ✓

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equal to 14,0 kcal/mole. It could be observed that the rate of volatilization of phenyl- β -naphthylamine decreases in accordance with the following order of polymers: polyethylene > fluororubber > SKB > SRS-30 > SKN-26 > nairite. The rate of volatilization sharply falls with increasing density of the three-dimensional network of the vulcanizate and also declines in the presence of a filler. The proposed mechanism of this volatilization process was confirmed by corresponding theoretical calculations, as a result of which the equation

$$\frac{c}{c_0} = 1 - e^{-\frac{m}{R}t} \quad (13)$$

(c - amount of ingredient volatilizing during the period t; c₀ - initial amount of ingredient in the rubber (percent by weight); m - constant; R - thickness of rubber plate (in cm)) could be found. The vulcanisates used to

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D034/D003

Volatilization of Ingredients from Polymers

show the rate of volatilization in dependence on the three-dimensional network of rubber specimens were prepared by treating 1 mm thick caoutchouc plates with X-ray tubes for radiochemical investigations of the type TRTs-ZA (developed by the Institut fizicheskoy khimii AN SSSR - Institute of Physical Chemistry AS USSR), under nominal working conditions of the tubes of 80 kw and 200 ma. There are 1 diagram, 8 graphs and 18 references, 10 of which are Soviet, 7 English, and 1 German.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti, Moskva (Scientific Research Institute of the Rubber Industry, Moscow)

SUBMITTED: December 7, 1958.

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S/080/60/033/005/008/008

AUTHORS: Kuz'minskiy, A.S., Gol'dfarb, Ya.L., Fedorov, B.P., Zenchenko,
~~A.I., Kogerman, A.P.,~~ Gorushkina, G.I., Angert, L.G.

TITLE: The Synthesis of Some Thiophene¹ Derivatives and the Study of
 Their Behavior as Rubber Ingredients (Accelerants and Anti-
 oxidants). Communication 2.

PERIODICAL: Zhurnal prikladnoy khimii, 1960, Vol 33, No 5, pp 1182 - 1187

TEXT: Some azomethines of the thiophene series are accelerants of the
 vulcanization process [Ref 1], some of them being also antiseptics [Ref 2]
 which is important for the cable industry. The most suitable azomethines
 are those containing hydroxyl groups. Other substances of this type were
 synthesized, therefore, which differed only in the position of the hydroxyl
 groups. The following substances were synthesized: bis-[2-thenylidene]-
 hydrazine, bis-[5-methyl-2-thenylidene]-hydrazine, bis-[2-thenylidene]- μ -
 phenylenediamine, 5'-methyl-2'-thenylidene-6-amino-2-mercaptobenzothiazole,
 5-methyl-2-thenylidene-o-aminophenol and 2'-oxybenzylidene-2-thenylamine,
 as well as two new sulfides: [β -oxyethyl]-2-thenylsulfide and 2-thenyl-
 [n-oxyphenyl]-sulfide. The two sulfides mentioned and 2'-thenylidene-6-

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s/080/60/033/005/008/008

The Synthesis of Some Thiophene Derivatives and the Study of Their Behavior as Rubber Ingredients (Accelerants and Antioxidants). Communication 2.

amino-2-mercaptobenzothiazole and 6-amino-2-mercaptobenzothiazole are accelerants, but their efficiency is less than that of mercaptobenzothiazole. It was evident that the hydroxyl group positively affects the accelerating action of the compounds, if it is located in the para-state of the benzene ring. The introduction of molecules of mercaptobenzothiazole of the amino-group into the benzene ring decreases the efficiency of the compound. A further complication of the molecule decreases the efficiency still more. The cause of these phenomena is not known at the present time. The principal role in the accelerating action of the compounds considered is played by the hydroxyl group.

There are 4 tables and 5 references: 2 Soviet, 2 English and 1 German.

SUBMITTED: August 20, 1959

Card 2/2

S/020/60/135/006/028/037
B004/B056

AUTHORS: Lyubchanskaya, L. I. and Kuz'minskiy, A. S.

TITLE: The Destruction of Molecular Chains and the Decomposition of Cross Links in the Aging of Vulcanizates

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 6, pp. 1436 - 1438

TEXT: It is the purpose of the present paper to clear up the problem as to what structural elements of vulcanizates undergo aging. The chemical relaxation of the strain of various vulcanizates was investigated. 1) Natural rubber. 2) КМБ (SKB) synthetic rubber, the cross links of which either a) consisted for the most part of monosulfide bonds, or b) for the most part of polysulfide bonds. For monosulfide cross links it was found that the kinetic curves for both natural rubber and SKB follow the equation $\sigma_t = \sigma_0 \exp(-kt)$. The constants of the reaction rate for natural rubber are $1.54 \cdot 10^{-3} \text{ h}^{-1}$, and for SKB, $2.1 \cdot 10^{-4} \text{ h}^{-1}$. Reduction of oxygen pressure from atmospheric pressure to 1 mm Hg lowers the reaction rate to

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The Destruction of Molecular Chains and the S/020/60/135/006/028/037
Decomposition of Cross Links in the Aging of B004/B056
Vulcanizates

1/5. It follows herefrom that the chemical relaxation in this case is caused by oxidative decomposition of the polymer chains. In polysulfide cross links, on the other hand, the relaxation rates for both kinds of rubber are similar: natural rubber: $4.2 \cdot 10^{-2} \text{ h}^{-1}$; SKB: $3.1 \cdot 10^{-2} \text{ h}^{-1}$. Removal of oxygen is without influence. Herefrom, the following conclusions are drawn. In the aging process of vulcanizates two competing reactions occur: a) oxidative destruction of the molecular chains of the polymer; b) thermal decomposition of the sulfide cross links. In the case of firm cross links (monosulfide), reaction a) predominates. The relaxation rate then depends on the oxidizability of the polymers and on the concentration of oxygen. If, however, the network of the vulcanizate is formed by polysulfide cross links, whose thermal decomposition is stronger by one order of magnitude than the oxidative destruction, reaction b) will predominate. There are 2 figures and 5 references: 3 Soviet and 4 US.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti
(Scientific Research Institute of the Rubber Industry)

PRESENTED: July 6, 1960, by P. A. Rebinder, Academician

SUBMITTED: June 30, 1960

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25268

S/190/61/003/007/012/021
B101/B22015.9205

AUTHORS: Kuz'minskiy, A. S., Goldovskiy, Ye. A.
TITLE: Study of the oxidation of polydimethyl siloxane rubber
PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 7, 1961,
1054-1061

TEXT: The aim of the present study was to obtain quantitative data on the processes occurring during oxidation of linear high-molecular polydimethyl siloxanes. The oxidation was effected by passing purified oxygen with 40 ± 1.5 ml/min through a reaction vessel containing the weighed portion (0.15 - 0.6 g) of the rubber film. The reaction vessel was maintained at constant temperature in a boiling liquid (diphenyl, alpha bromonaphthalene or diphenylamine). The volatile products leaving the rubber were carried by the O_2 into the zone of combustion ($950-1000^\circ C$), where they burned to SiO_2 , CO_2 , and H_2O . The SiO_2 was collected in a quartz tube filled with asbestos, the CO_2 and H_2O in Pregl's absorbers filled with anhydrous and ascharite. The oxygen associated to the

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Study of the oxidation of ...

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S/190/61/003/007/012/021
B101/B220

polymer was calculated from the oxygen balance. The maximum limit of error was 1-2% for the determination of C and H₂; 1-15% for Si; and 1-3% for O₂. The solubility of the rubber was determined in toluene. The swelling maximum in toluene was measured by means of a torsion balance, after washing out the soluble part. The number of cross links was calculated from the swelling maximum according to the equation by P. Flory and J. Rehner (see below), μ being 0.465. The molecular weight M of the soluble fraction was calculated from the intrinsic viscosity of the toluene solution according to $[\eta] = 2.15 \cdot 10^{-4} M^{0.65}$. The tests were made with purified and commercial CKT (SKT) rubber. The purified rubber was a high-molecular fraction of polydimethyl siloxane, $M \approx 900,000$, obtained by precipitating the 1% benzene solution of commercial rubber by means of methanol. The low-molecular fractions were separated from the commercial rubber by heating to 90-100°C under a pressure of 10^{-2} - 10^{-3} mm Hg. In the first series of tests, the destruction of the rubber was determined as function of the length of heating. In the second series, the kinetics of the destruction were determined by replacing the absorbers in certain intervals. This series gave more exact results. The kinetic curves for

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the splitting-off of methyl groups at 258, 280, and 302°C are shown in Figs. 2,3. Results: 1) The rate of splitting-off of CH₃ groups at 280°C increases with increasing thickness of the rubber film (from 0.25 to 0.6 mm). In case of thicker films (0.85 mm) the rate of splitting-off decreases, because the diffusion of the O₂ is impeded; 2) Addition of 0.5-1% di-β,β'-naphthyl-p-phenylene diamine which is used in hydrocarbon rubbers as antioxidant reduces the rate of the splitting-off of CH₃.

Moreover, also the splitting off of volatile organosilicon compounds and the cross linking are delayed. 3) The H/C ratio amounted to 2.5-2.9 in the volatile products (after deduction of the content in organosilicon compounds). Apparently, a part of the H₂ of the CH₃ groups split off is bound again by the polymer in form of OH groups. 4) The kinetic curves of the splitting-off of volatile organosilicon compounds have the shape of an S (Fig. 4). 5) The degree of cross linking at 258°C is directly dependent on the number of CH₃ groups split off and is, thus, influenced neither by the rate of the splitting-off of CH₃ nor by that of the organosilicon compounds. 6) In the initial stage of oxidation the ratio

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cross-links; CH_2 groups split off is very small (0.02), but increases later on (0.3 for 12 mole% CH_2 split off). This is explained by formation of intramolecular bonds (cyclization). There are 5 figures and 16 references: 10 Soviet-bloc and 6 non-Soviet-bloc. The 3 most important references to English-language publications read as follows: D.C. Atkins, C.M. Murphy, C.E. Saunders, Industr. and Engng. Chem., 39, 1395, 1947; P. Flory, J. Rehner, J. Chem. Phys., 11, 521, 1943; A.M. Bueche, J. Polymer Sci., 15, 105, 1955.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti
(Scientific Research Institute of the Rubber Industry)

SUBMITTED: October 17, 1960

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28799

15.8620

S/138/61/000/009/003/011

A051/A129

11.2320

AUTHORS: Kuz'minskiy, A. S., Abramova, T. Ya., Zuyeva, M. V.

TITLE: Radiation vulcanization of butadiene-nitrile rubbers

PERIODICAL: Kauchuk i rezina, no. 9, 1961, 12 - 15

TEXT: The Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti (Scientific Research Institute of the Rubber Industry) has carried out a laboratory study on conditions for radiation vulcanization of butadiene-nitrile rubber mixes and the properties of the vulcanizates obtained. The best results were achieved with two-component mixes consisting of rubber and carbon black. Channel black proved to be the most efficient filler. The optimum radiation dose was 15 - 20.10⁶r. Increase in the acrylonitrile content in rubber increased the tensile strength and relative elongation of the vulcanizates, but reduced their swelling in gasoline-benzene mixtures. Softeners, such as paraffin and stearin, improved the strength properties of the vulcanizates. Comparison of the properties of irradiation and sulfur vulcanizates of CKH-26 (SKN-26) and SKN-40 rubbers showed that the former have a higher elasticity, a lower melting point and a higher coefficient of low-temperature resistance. The two types of vulcanizates exhibit si-

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AO51/A129

Radiation vulcanization of butadiene-nitrile rubbers

milar strength, hardness, swelling and abrasive properties. The laboratory results were confirmed by industrial tests of packing rings made with irradiation vulcanizates. The use of such vulcanizates in the manufacture of industrial rubber products makes possible a temperature range of -60 to +120°C for the application of butadiene-nitrile rubbers instead of -40 to +100°C. There are 4 tables, 3 figures and 7 references; 3 Soviet-bloc and 4 non-Soviet-bloc. The references to the English-language publications read as follows: A. Chapiro, Ind. Plast. Mod., 9, no. 1, 41 (1957); R. Harrington, Rubb. Age, 77, 865 (1955); D. J. Harmon, Rubb. Age, 86, no. 2 (1959); W. Jackson, D. Hale, Rubb. Age, 77, 865 (1955). ✓

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti (Scientific Research Institute of the Rubber Industry)

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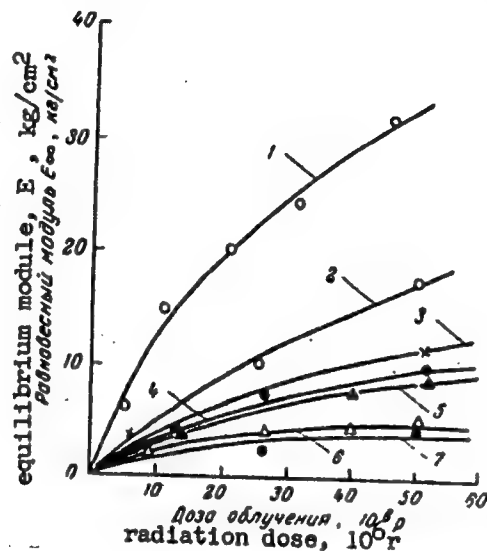
28799

Radiation vulcanization of butadiene-nitrile rubbers

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Fig. 1. Relation of the magnitude of the equilibrium module of various rubbers to the radiation dose

Legend: 1 - SKN-40
2 - SKN-26
3 - SKB
4 - SKT
5 - SKS-30
6 - SKF-32
7 - NR



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20249

15.8600 only 2209

S/138/61/000/001/009/010
A051/A029

AUTHORS: Kuz'minskiy, A. S., Oksent'yevich, L. A.

TITLE: The II All-Union Conference on Radiation Chemistry

PERIODICAL: Kauchuk i rezina, 1961,²⁰ No. 1, pp. 53-55

TEXT: On October 10 - 14, 1960, the II Vsesoyuznoye soveshchaniye po radiatsionnoy khimii (II All-Union Conference on Radiation Chemistry) took place in Moscow, called together by the USSR State Committee on Chemistry at the Council of Ministers. Academician A. P. Vinogradov opened the meeting and stressed the significance of radiation chemistry as a new branch of science which studies the energy of the atom. Its development follows two lines: 1) industrial application of nuclear emissions, 2) extensive theoretical studies of the chemical transformations taking place under the action of nuclear emissions. N. A. Bach, Chairman of the organizing committee of the conference, underlined the importance of radio chemical investigations as the basis of radiation-resistant materials and for the application of nuclear emissions when conducting directed chemical processes. Special interest was expressed in the possibility of radiation polymerization at low

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temperatures. G. V. Uvarov, Vice Chairman of the State Committee on Chemistry, said that radiation polymerization of ethylene, radiation vulcanization of special rubbers and telomerization will be introduced into the industry. There were five sections of the conference: 1) the action of emissions on aqueous solutions and 2) on organic substances, 3) radiation polymerization and action of emissions on polymers, 4) action of emissions on a solid body, 5) routine questions of radiation-chemistry investigations. A total of 120 papers were submitted (representing 35 institutions). Some of the more important papers submitted are mentioned: A. D. Abkin gave a short characteristic outline of the radiation polymerization process. The process takes place according to the ionic mechanism. In the process of radiation polymerization in an emulsion the independence of the general rate of polymerization on the temperature is underlined. The rate of polymerization is proportional to the intensity of the emission in the first degree. Cases of the combined polymerization of isobutylene and vinylidene chloride, styrene and methylmethacrylate were discussed. The significant role in ionic polymerization is said to be played by the surface. Yu. L. Khmel'nitskiy, Ye. M. Kononova and V. V. Nesterovskiy dealt with the radiation polymeriza-

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tion of propylene, isobutylene and one of the amylenes (2-methylbutene-2) at various temperatures and at various degrees of purity of the monomer. It was shown that with a drop in the temperature and an increase in the degree of purity of the monomer the polymer yield and the average molecular weight increases. I. P. Barkalov, A. A. Berlin, V. I. Gol'danskiy, B. G. Dzentiyeva, et al., presented a study on the kinetics and mechanism of radiation polymerization of acetylene hydrocarbons. Ye. V. Volkova, A. F. Forkin, A. D. Sorokin and V. M. Belikov handled the question of radiation polymerization of trifluorochloroethylene and tetrafluoroethylene. A study is being conducted at present on the kinetics of the process in the gaseous phase under the action of beta-emissions of Sr^{90} . The paper of Kh. U. Usmanov, U. N. Musayev and R. S. Tillayev submitted the data of copolymerization of acrylonitrile with methylfurane (silvane), copolymers were obtained through the grafting of polyvinylchloride-acrylonitrile, polyvinylchloride-silvane, perchlorovinyl-silvane systems; R. S. Klimanova, V. I. Serenkov and N. S. Tikhomirova investigated the copolymerization by grafting with styrene and polyethylene. The paper of B. L. Tsetlin, S. R. Rafikov, L. I. Plotnikov and P. Ya. Glazunov dealt with the radiation grafting of various polymer chains to the surface of mineral particles and also to carbon black.

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V. L. Karpov and Yu. S. Lazurkin gave a general characteristic outline of the processes taking place under the action of nuclear emissions. L. G. Gurvich developed a theory of radiation destruction of linear polymers. Several papers were dedicated to the investigation of the mechanism of radiation-chemical transformations in polymers: Yu. D. Tsvetkov, Ya. S. Lebedev and V. V. Voyevodskiy - on the method of electronic paramagnetic resonance used for the study of the kinetics of recombination of the fluoro-alkyl and peroxide radicals formed in teflon under the action of gamma-emissions of Co^{60} ; A. G. Kiselev, M. A. Mokul'skiy, Yu. S. Lazurkin - on the investigation of radicals occurring when irradiating various orientated polymers in a reactor or in a beta-source; N. Ya. Buben, A. T. Koritskiy and V. N. Shamshev on the investigation of the effect of admixtures (CCl_4 , benzene, toluene, CS_2) on the kinetics of accumulation of radicals in paraffin and polyethylene under the action of fast electrons; N. A. Slovokhotov, A. T. Koritskiy, et al. - on the structure of polyethylene irradiated in liquid nitrogen with fast electrons using the method of infra-red spectroscopy. V. G. Nikol'skiy and N. Ya. Buben - on the thermo-luminescence of polyethylene, paraffin, teflon, rubbers and certain aromatic hydrocarbons irradiated

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with fast electrons, in order to determine the structural transformations in these compounds; G. P. Ushakov, Yu. S. Lazurkin and Yu. A. Gushcho - on an investigation of the effect of the phase state of polyethylene of low pressure on its physical and mechanical properties when irradiated in a reactor; V. L. Karpov, S. S. Leshchenko and E. E. Finkel' - on the effect of various additions on the change of the strength properties of polyethylene irradiated in a Co^{60} source during the process of thermal aging. Some papers were dedicated to the action of radiation on rubbers. B. A. Dogadkin, Z. N. Tarasova, M. Ya. Kaplunov, et al. read on the effect of sulfur on the kinetics of radiation structuralizing of natural and butadiene-styrene rubbers and the properties of the irradiated vulcanizates; B. A. Dogadkin, V. I. Gol'danskiy, Z. N. Tarasova, M. Ya. Kaplunov, et al. - on a method for vulcanizing various samples of rubbers on a linear impulse accelerator and on the kinetics of formation of transverse bonds and the structural changes of the natural, butadiene-styrene and carboxylic rubbers, when irradiated by a beam of 2 Mev-energy electrons; I. Ya. Poddubnyy and S. V. Aver'yanov - on the radiation vulcanization of siloxane rubbers, where the vulcanization conditions were selected for various polysiloxanes ensuring the production of rubbers with a very high thermal stability. A. S. Kuz'minskiy,

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The II All-Union Conference on Radiation Chemistry

L. S. Fel'dshteyn, Ye. V. Zhuravskaya and L. I. Lyubchanskaya - on the laws of radiation aging of deformed rubbers based on natural rubber, CKC-30 (SKS-30), CK5 (SKB) and CKH-26 (SKN-26); G. A. Blokh, V. L. Karpov, Yu. M. Malinskiy, L. P. Ol'ghanskiy and M. S. Khloplyankin - on the action of the gamma-emission of Co^{60} on various cable rubbers and constructions. It was established that after irradiation with a 50 - 100 Mrad dose the main physico-mechanical and electro-insulating properties are impaired. The question of distribution and energy transformation of emissions in organic systems and the mechanism of radiochemical processes were discussed. At the final meeting it was pointed out that the three years since the first conference were characterized by: 1) noticeable general growth of the radiochemical investigations, 2) extensive increase in research and investigations into the mechanism of these processes, 3) appearance of many papers on the action of radiation on a solid body, 4) the application of physics and complex methods of investigations, such as electronic paramagnetic resonance, chromatographic, electrical, spectral and other methods. It was decided to conduct a meeting in 1961 on the industrial application of radiochemical processes, in 1962 on general theoretical questions and studies

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The II All-Union Conference on Radiation Chemistry

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on the mechanisms of radiochemical processes. In 1963 the III All-Union Conference on Radiation Chemistry will be convened.

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FEL'DSHTAYN, L.S.; KHANIN, S.Ye.; FRENKEL', R.Sh.; KUZ'MINSKIY,
A.S.

- . Vulcanization of rubber with mercaptan in the presence of carbon blacks. Kauch. i rez. 20 no.8:28-32 Ag '61. (MIRA14:8)

1. Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti.

(Vulcanization)

KUZ'MINSKIY, A.S.; ABRAMOVA, T.Ya.; ZUYEVA, M.V.

Radiation vulcanization of butadiene-nitrile rubbers. Kauch.
i rez. 20 no.9:12-15 S '61. (MIRA 15:2)

1. Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti.
(Vulcanization)
(Rubber, Synthetic)

30462

S/138/61/000/011/002/007
A051/A126

5.4600 (a/no 1273)

AUTHORS: Kuz'minskiy, A. S., Ruzer, L. S., Sunitsa, L. L.

TITLE: Apparatus with a source of γ -emission Co^{60} , of 16,000 g-equiv. radium for radiation-chemical investigations of synthetic and natural rubbers

PERIODICAL: KAUCH. I REZ. 20 no 11, 8-10, N'61.

TEXT: The Scientific Research Institute of the Rubber Industry (NIIRP) is at present engaged in a study of the effect of ionizing radiation on the properties of rubbers and rubber-like materials, in addition to work on the modification of various rubbers and their ingredients. A new apparatus with a cobalt⁶⁰ source, having a 10,000 curie (16,000 g-equiv. of radium) activity was put into operation at the institute in January 1959. It was based on the efforts of the Geneva 1958 International Conference for the Peaceful Utilization of Atomic Energy, and on papers presented by Soviet Scientists (Vol. 4, Moscow, 1959, p. 266). The apparatus (Fig. 1), installed in an underground building with concrete walls, is covered with a layer of hydroinsulating material on the outside, and tiles on the inside, concrete ceiling, 1.5 m thick, having an earth layer, 0.5 m thick. The emission chamber is separated from the labyrinth by a protective concrete rod, 1.25 m thick. The control panel is located in the control room to move by means of a hoisting mechanism the source from its storage position to a working position so that the

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Apparatus with a source of...

samples may be irradiated. The physico-chemical control desk is also located in the control room. The elevation of the container with the samples of the Co^{60} from its storage to a working position is accomplished with compressed air from the control panel through a flexible tube, directed to the float of the hoisting mechanism. The well containing the source is covered with a stainless steel top consisting of two halves with a groove in the middle. A table for the irradiation of the samples with a cylindrical protective container, is located over this top. The physico-chemical control desk contains the instruments for measuring the various parameters (temperature, pressure), characterizing the processes in the irradiated samples: electronic potentiometers ЭПП-09 (EPP-09), ЭПВ-01 (EPV-01). A video-receiving apparatus of the industrial television set ПТУ - ОМ (PTU-OM), with a transmission chamber located in the labyrinth is also located on the physico-chemical control desk. The energies of the emission dosages within the protective container and in the external part of the sample are measured by the ferrosulfate chemical dosimeter method. The average energy of the dose within the protective container, in a volume of 1 liter, is equal to 353 r/sec. In the external area of the sample, the dose energy varies from 180 to 20 r/sec. The blocking circuit opens the door of the chamber under the four following conditions: 1)

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A051/A126

Apparatus with a source of...

the air is let out from the hoisting reservoir, 2) the electrical upper end switch of the transporting mechanism is shut off, 3) the lower end switch is turned on, 4) the level of emission in the labyrinth at the position of the "cactus" transmitter is less than 0.1 r/sec. The dosimetric instrument "cactus" has a sonic and light signalling system indicating the elevation of the given level of emission in the labyrinth. The described apparatus led to the development of the principles for radiation vulcanization of silicon, fluoro- and nitrile rubbers, as well as the commercial rubber products produced from the latter. Based on the results of the conducted radiation-chemical investigation a radiation vulcanization shop was designed. The mechanism of the radiation agent and the action of anti-rads in rubbers have been investigated to raise their radiation stability. There are 2 figures and 1 photograph. X

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti (Scientific Research Institute of the Rubber Industry)

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KUZ'MINSKIY, A., doktor khimicheskikh nauk, prof.; BASS, S., inzh.

Lengthening the life of polymers. Tekh.mol. 29 no.6:15 '61.
(MIRA 14:7)

(Plastics)

S/020/61/136/004/015/026
B016/B075

AUTHORS: Fel'dshteyn, L. S., Reytlinger, S. A., and Kuz'minskiy, A. S.

TITLE: The Problem of Crystallizing Low-molecular Substances From
Solutions Into High Polymers

PERIODICAL: Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 4,
pp. 843 - 845

TEXT: The authors attempted to find the reasons for an undesirable phenomenon, the so-called "efflorescence" (Ref.1), i.e., the formation of oversaturated solutions of low-molecular substances in high-polymer solvents. The former mostly crystallize on the interface polymer - gas. The system sulfur (2g) - polybutadiene (100 g) (CKE-30 (SKB-30)) served as test object. By using S^{35} (Ref.2), the relative quantity of sulfur crystallized on the polybutadiene surface was determined. Platelets, 2 mm thick and 26 mm in diameter, were obtained by pressing a mixture of the two components for 60 min at 100°C in a cellophane foil. Before measuring the activity by means of an end-window counter, the cellophane foil was removed from one side. Already 24 hours after removing the cellophane

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The Problem of Crystallizing Low-molecular
Substances From Solutions Into High Polymers

S/020/61/136/004/015/026
B016/B075

foil, a considerable increase in activity was observed (Fig.1). The authors explain this phenomenon by sulfur crystallization on the surface, since a concentration gradient had formed. The side covered by cellophane showed no increase in activity even after additional pressing. When storing the specimens wrapped in cellophane for a longer period efflorescence decreased until it completely vanished. On the strength of these data, the authors conclude that equilibrium was established due to crystallization inside the specimen. Crystallization sets in immediately after removing the cellophane foil. The time necessary for establishing equilibrium is determined by the diffusion rate of the sulfur from inside the specimen. When the cellophane was removed from none of the two surfaces even after 60 days equilibrium was not established. Therefore the authors concluded that crystallization proceeds considerably slower inside the specimen than on its surface. The quick establishment of equilibrium in the case of strong oversaturation indicates that the formation of seed crystal is inhibited. By admixing pulverized metallic selenium, the authors succeeded in initiating the crystallization inside the specimen. Selenium is insoluble in rubber, but since it is isomorphous with sulfur it easily forms mixed crystals with the latter. The authors

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The Problem of Crystallizing Low-molecular
Substances From Solutions Into High Polymers

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B016/B075

refer to the processes during crystal formation (Ref.4) and state that the difference between the diffusion coefficient of the dissolved substance and the self-diffusion coefficient of the polymer solvent inhibits the formation of crystallization centers inside the specimen. Plasticizers increase the mobility of polymer molecules and the probability of crystallization inside the specimen. Thus, sulfur does not effloresce in factices (Ref.2). There are 3 figures, 1 table, and 6 references. 4 Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti
(Scientific Research Institute of the Rubber Industry)

PRESENTED: July 8, 1960, by P. A. Rebinder, Academician

SUBMITTED: June 30, 1960

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15.9300

29821
S/020/61/140/006/018/030
B103/B101

AUTHORS: Kuz'minskiy, A. S., and Goldovskiy, Ye. A.

TITLE: Some characteristics of the oxidation process of polydimethyl siloxane rubber

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 140, no. 6, 1961, 1324-1326

TEXT: The thermal oxidation of a purified high-molecular fraction of polydimethyl siloxane rubber (I) (molecular weight ~900,000) was studied. The total amounts of C, H₂, and Si were determined by microanalysis in compounds separated from I on oxidation. Principles of these methods: carefully purified O₂ is passed through a vessel containing the polymer to be oxidized, with a constant velocity (40 ± 1.5 ml/min). O₂ carries the products separated from the polymer into the combustion zone, where they are oxidized completely to H₂O, CO₂, and SiO₂. The quantity of separated organosilicon compounds, related to polydimethyl siloxane, was calculated from the quantity of SiO₂ recovered. The number of split-off methyl

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B103/B101

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groups was ascertained from the difference between the C quantity of all volatile and that of the volatile organosilicon compounds. Partial pyrolysis of the organosilicon compounds separated from the polymer occurred during the test in N₂ stream in the quartz tube (at 950°C). The pyrolytic products were oxidized in O₂ current to SiO₂ after completion of the test.

An anomalous phenomenon was established on filmlike samples: at 250 - 300°C, the splitting-off of methyl groups in O₂ current is accelerated with increasing film thickness, consequently also the oxidation underlying the splitting-off is accelerated. This takes place only up to a certain ("optimum") film thickness. On oxidation of the polymer in air, this thickness is: 0.6 mm at 280°C; 0.3 mm at about 300°C; 0.75 mm at 270°C; 2.5 mm at 250°C; and more than 4 mm at 230°C. The oxidation rate of methyl groups is a function of two competitive factors: 1) Formation of volatile compounds (possibly formaldehyde) which accelerate the process. With increasing film thickness, a steadily rising percentage of such compounds reacts before leaving the film, thus accelerating the oxidation. This assertion is confirmed by the fact that a film of 1 of 0.25 - 0.5 mm

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thickness superimposed on a second I film is more rapidly structured than a film of equal thickness which is applied directly on a quartz base. Furthermore, a film of about 1μ thickness on a KBr base is not oxidized noticeably, even when heated for 36 hr at 300°C in air. Infrared spectroscopy revealed the following fact: when glass is covered with a film of 1μ and a second film of 0.5 mm thickness of I, the film of 1μ thickness will be oxidized already after heating at 300°C for 6 hr. 2) Retardation of O_2 diffusion in the film. In films of adequate thickness (about 0.8 mm), the lower part contacting the base is structured more slowly at 280°C than the upper part. This difference increases with growing film thickness. When the "optimum" film thickness is exceeded, the effect of factor 2) becomes stronger than that of factor 1). Thus, the oxidation rate decreases again with increasing film thickness. The effect of factor 1) is one reason to presume the chain character of the oxidation of I. A further additional prove is the abrupt retardation of the splitting-off of methyl groups (by 1.5 orders of magnitude), when 0.5 - 1% of di- β,β' -naphthyl-p-phenylene diamine and 50 parts by weight of Y-333 (U-333) powdered silica gel are added. It has been found that the splitting-off of low-molecular organosilicon compounds in the initial period is significantly accelerated

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by oxygen. Possibly, the accelerating O_2 effect is due to the oxidation of methyl groups. The two last-mentioned additions delay the splitting-off of side groups and reduce, moreover, the separation of organosilicon compounds. No connection exists, however, between the quantities of methyl groups and organosilicon compounds split-off. There are 3 figures and 11 references: 5 Soviet and 6 non-Soviet. The four most recent references to English-language publications read as follows: E. G. Rochow, An Introduction to the Chemistry of the Silicones, N. Y., 1951; L. C. Scala, W. M. Hickam, Ind. and Eng. Chem., 50, 1583 (1958); W. J. Lewis, J. Polym. Sci., 33, 153 (1958); 37, 425 (1959).

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti
(Scientific Research Institute of the Rubber Industry)

PRESENTED: May 30, 1961, by S. S. Medvedev, Academician

SUBMITTED: May 25, 1961

Card 4/4

KUZ' MINSKIY

USSR

DOGADKIN, B. A., and TARASOVA, Z. N., Moscow
Institute of Fine Chemical Technology named
M. V. Lomonosov [1961 position] - "Influence
of vulcanisation structures on physical and
mechanical properties of vulcanisates"
(Session II)

13

KUZ' MINSKIY, A. S., LYUBCHANSKAYA, L. I.,
FEL'DSHTEIN, L. S., Scientific Research Institute
of Rubber Industry, Moscow [1960 locations] -
"Influence of mechanical stresses on the ageing
of vulcanised rubbers" (Session VIII)
NOVIKOV, A. S., GILINSKAYA, N. S., DYUMAYEVA, T. N.,
GRIBACHEVA, A. V., RUDEL'MAN, Z. N., and
GALIL-OGLY, F. A., Scientific Research Institute
of Rubber Industry, Moscow [1961 locations] -
"Investigation of amine vulcanisation of
SKF-26 fluoroco-polymer" (Session II)
REZNIKOVSKIY, M. M., and BRODSKIY, G. I.,
Scientific Research Institute of Tire Industry,
Moscow - "Special features of the mechanism of
abrasion of high-elastic materials" (Session V)

Report to be submitted for the 4th Rubber Technology Conference,
London, England, 22-25 May 1962.

S/844/62/000/000/098/129
D234/D307

AUTHORS: Kuz'minskiy, A. S., Fel'dshteyn, L. S., Zhuravskaya, Ye.
V. and Lyubchanskaya, L. I.

TITLE: Radiation ageing of rubbers in stressed state

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 576-580

TEXT: Stress relaxation was investigated by means of an axial compression relaxometer described in a previous paper. The compression degree was 20%. Specimens were irradiated by a Co60 source, the dose being varied from 0.5 to 1 Mr/hr. The specimens consisted of vulcanized natural HK (NK), butadiene-nitril (KN-26 (SKN-26), sodium-butadiene (KB (SKB) and butadiene-styrene (KC-30 (SKS-30) rubbers. With respect to the velocity of relaxation, NK > SKV > SKS-30 > SKN-26, and with respect to that of residual deformation, SBK > NK > SKN-26 > SKS-30. Structurization and destruction outputs are compared. Presence of anti-radiation substances (N-phenyl-N'-

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cyclohexyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine) in the quantity of 5% by weight did not affect the chemical relaxation rate but slightly affected the rate of accumulation of residual deformation and decreased considerably the rate of structuration. The rate of residual deformation was decreased by anti-radiation substances only in the case of irradiation in air but not in vacuum. There are 4 figures and 1 table. ✓

ASSOCIATION: NII rezinovoy promyshlennosti (NII of the Rubber Industry)

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S/138/62/000/001/006/009
A051/A126

15.9300
11.2211

AUTHORS:

Lyubchanskaya, L.I.; Fel'dshteyn, L.S.; Kuz'minskiy, A.S.

TITLE:

Rubber aging in the strained state

PERIODICAL: Kauchuk i rezina, no. 1, 1962, 23 - 29

TEXT:

The authors investigated the major law sequences in the process of chemical relaxation of tension and studied the effect of various composition factors. The accumulation kinetics of residual deformation and changes of the equilibrium standard (proportional to the number of transverse chemical bonds) were further examined. Natural and sodium-butadiene rubber were chosen as the experimental material. An axial compression relaxometer was used to test the chemical relaxation of tension. It was found that the rate of the relative drop in tension does not depend on the compression degree within the 20 to 5% deformation range. The tension drop is the result of the break in the bonds under tension; the accumulation of the residual deformation is determined primarily by structuring. According to the rate increase of tension relaxation, the vulcanizates are arranged in the following sequence: thiuram < vulcanizate with sulfur and captax < vulcanizate with sulfur and diprenylguanidine. The rate con-

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Rubber aging in the strained state

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stants of the relaxation process, calculated according to the mono-molecular reactions are: 1 : 6 : 39. With the presence of transverse bonds in the vulcanizates, the reactivity of the polymer, with respect to the oxygen, strongly affects the ratio of tension relaxation. Data obtained further revealed that: 1) in aging of the deformed vulcanizates there are two competing processes taking place - oxidizing destruction of the polymer's molecular chains, and a thermo-mechanical decomposition of the transverse sulfur bonds. 2) In the presence of strong transverse mono- or disulfide bonds in the vulcanizates, the chemical relaxation of tension is determined by the oxidizing destruction of the molecular chains of the polymer and thus, the relaxation rate depends in this case on the reactivity of polymers and oxygen concentration. 3) Various carbon blacks (channel, furnace, thermal and lamp) increase the rate of chemical relaxation in the following sequence: channel > furnace > lamp > and thermal. The nature of the transverse bonds appears to be the main factor, determining the behavior of rubber in aging under conditions of static deformations. The selection of the appropriate polymer followed by the filler range next in importance. It is concluded that in rubber aging in the presence of oxygen, the tension relaxation process is determined by a thermal break of the transverse bonds for rubbers with polysulfide bonds and by thermo-oxidizing destruction of the polymer in vul-

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Rubber aging in the strained state

canizates with strong transverse bonds. There are 8 figures.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti (Scientific Research Institute of the Rubber Industry)

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34136

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A051/A126

11.2210
15.8000

AUTHORS: Kuz'minskiy, A.S., Bass, S.I.

TITLE: Conference on aging and stabilization of polymers

PERIODICAL: Kauchuk i rezina, no. 2, 1962, 50 - 52

TEXT: The conference, convened by the AS USSR, the USSR Council of Ministers, State Committee on Chemistry and the Ministry of Higher and Intermediate Special Education of the RSFSR, took place at the Institute of Chemical Physics of the AS USSR, from November 14 - 17, 1961. Over 200 delegates participated and 62 papers were presented. Academician V.A. Kargin spoke on the subject of aging and stabilization of rubber, various plastics, fibers, dye and lacquer coatings, and he stressed the use of fillers and polymer substances as stabilizers. V.B. Miller, Yu.A. Shlyapnikova (IKhP AS USSR) discussed certain law sequences of oxidation destruction of polypropylene in the presence of antioxidant-aromatic amines and phenols. The conclusion that inhibitors initiate the oxidizing process of the polymer is confirmed. M.V. Neyman and A.L. Buchachenko (IKhP) spoke on the results of an investigation of stable radical products, formed in thermal and catalytic decomposition of hydroperoxides in the presence of various anti-

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Conference on aging.....

oxidants. G.I. Likhtenshteyn (IKhF) presented the results of a theoretical investigation of the effects of inhibitors on the oxidation of hydrocarbons. Several papers dealt with the study of the synergetic effect of inhibitor mixtures. A.F. Lukovnikov, P.I. Levin and M.S. Khlopyankina (IKhF) investigated the synergism of mixtures of certain secondary amines with various sulfur-containing compounds in the process of oxidation of isotactic polypropylene at 200°C. An investigation of the behaviour of stable radicals of diphenylamine, phenyl- β -naphthylamine, etc., in the presence of a number of sulfur-containing compounds, with the decomposition of the hydroperoxides using the EPR spectra was conducted by M.S. Khlopyankina, A.L. Buchachenko, (IKhF). A.B. Gagarina, Z.K. Mayzus and N.M. Emanueliy, confirmed experimentally the existence of critical concentrations of inhibitors in liquid-phase oxidation of hydrocarbons, predicted by N.N. Semenov for slow chain reactions with degenerated branches. A.S. Kuz'minskiy and Yu.A. Goldovskiy (NIIRP) reported on certain laws of oxidation of polydimethylsiloxane rubber at 250 - 300°C. A discussion was given on the investigation of aging of methylvinylpyridine rubber and raw rubber, based on the latter, by L.G. Angert, A.I. Zenchenko and A.S. Kuz'minskiy, (NIIRP). The report of Z.A. Tarasova, I.I. Eytingon, L.G. Senatorskiy, T.V. Fedorova, G.I. Andronova and B.A. Degadkin (NIIShP), dealt with the results of an investigation on the action of

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certain thioamines, thiophenols and synergetic mixtures, based on the latter, during the process of vulcanization and in fatigue of NR, isoprene and butadiene-styrene rubber vulcanizates. The paper of G.L. Slominskiy, V.A. Kargin and Ye.V. Reztsova (INEOS AS USSR, NIIShP) concerned the problems connected with the transformation of macroradicals formed in high-elastic polymers under the action of mechanical tensions during processing service of these polymers. T.G. Degtyeva, I.K. Sedova and A.S. Kuz'minskiy (NIIRP) presented the results of an investigation of thermal decay (250 - 380°C) of the copolymer of trifluorochloroethylene with vinylidene fluoride. Yu.S. Zuyev and A.Z. Borshchevskaya (NIIRP) reported on the results of an investigation of corrosive cracking of deformed rubbers, based on carboxyl-containing butadiene-styrene rubber, [CKC-30-1 (SKS-30-1)], in solutions of HCl, CH₃COOH and ozone, and also of rubbers based on NR and nairite in ozone. A conclusion was drawn that the destruction mechanism of rubbers in aggressive media, in the deformed and non-deformed state, is not the same. The use of the condensation of aniline chloride with acetaldehyde as stabilizers of raw and synthetic rubber products was discussed by L.P. Zalukayev, T.I. Zheltukhina, L.Ya. Sinitsyna (VNIISK). Certain papers dealt with the results of a study on destruction and stabilization of polyolefines. Ye.N. Matveyev, et al. (NIIPP) investigated the oxidation of polypropylene at 120 - 170°C

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and showed the connection between the rate of oxygen absorption and property changes of polymers, both in the presence and absence of various stabilizers. The paper of V.D. Moiseyev and V.I. Suskin (IKhF) dealt with the theory on computing the rate of depolymerization, isomerization and transfer of the chain in thermal destruction of vinyl polymers using experimental data. V.S. Pudov and B.A. Gromov (IKhF) showed that the primary process in thermo-oxidation destruction of polypropylene is the formation of peroxides, the decomposition of which causes the formation of a complex mixture of the products of oxidation. N.V. Mikhaylov, et al., (VNIIV) made a study of certain stabilization features of polypropylene and fiber based on the latter, and analyzed the reasons for discrepancy in the induction periods of oxidation for the polymer and its fiber. P.I. Levin, P.A. Kirpichnikov, (IKhF) presented the results of their investigation of polypropylene stabilization with mixtures of phosphites and sulfur-containing compounds, not causing the appearance of a coloured polymer during the entire induction period. Certain possibilities of using the spectral methods for studying the aging processes of polymers were stressed by V.M. Chulanovskiy, (NIISHP). N.S. Yenikolopova, L.A. Dudina and L.V. Karmilova presented the results of an investigation on the thermal and thermo-oxidation destruction of polyformaldehyde. A.A. Berlin, et al., reported on the effect on the stability of polyvinylchloride polymers,

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with a system of conjugated links, produced in the polymerization of acetylene hydrocarbons, or in the splitting off of atoms or groups from the macro-molecules. S.R. Rafikov (INEOS, AS USSR), N.V. Mikhaylov (VNIIV) spoke on the thermal and thermo-oxidation destruction of polyamides. Several papers dealt with destruction and stabilization of condensed resins, photochemical destruction of intracellulose coatings, property changes of lacquer-dye coatings in aging, destruction and stabilization of cellulose ethers, radio-chemical transformation of polyethers, thermal destruction and stabilization of polydimethylsiloxane. A special meeting of the conference was devoted to the synthesis of new stabilizers: amines, screened phenols, phosphoro-organic compounds, light-stabilizers of the benzo-phenone row, derivatives of n-phenyleneamine, quinoline and phenol, as inhibitors of ozone aging of rubbers, etc. The importance of an all-sided study of the behaviour of real polymer materials under various conditions of storage, processing and service was emphasized. Resolutions were adopted to intensify the theoretical work on aging of real polymer systems, for unification of various methods for evaluating the aging process, and to increase publications on the problems of aging and stabilization of polymers. ✓

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A051/A126

159201

AUTHORS: Frenkel', R. Sh., Kuz'minskii, A. S., Fel'dshteyn, L. S., Khanin, S. Ye., Vinogradova, L. F.

TEXT: The effect of ingredients in rubber mixes on the structuralizing of butadiene-nitrile rubber

PERIODICAL: Kauchuk i rezina, no. 3, 1962, 10 - 12

TEXT: An investigation was conducted to determine the effect of ingredients other than altax, for example (in the absence of sulfur), on the process of thermal structuralizing in synthetic rubbers. Butadiene-nitrile rubber CKH-26 (SKN-26) (commercial) was used in the experiments in an air medium. The thermomechanical method was used to determine the initial temperature of the mixture structuralizing. Accelerators and activators of vulcanization have a significant effect on the rate of thermal structuralizing. The accelerators increase the rate of structuralizing and lower the initial temperature. At the addition of zinc oxide into the system rubber-altax decreases the initial temperature and increases the rate of structuralizing. Thus, it is thought that the zinc oxide serves as a catalyst in the process of thermal decomposition. Data on the reaction kinetics with

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The effect of...

iodine prove this supposition. The following conclusions are drawn: Certain fillers (gaseous and thermal carbon black) and accelerators (captax) increase the tendency to structuralizing of the mixtures based on butadiene-nitrile rubber. Those filled with gaseous carbon black, containing altax or captax, are particularly prone to structuralizing. Zinc oxide increases the structuralizing action of captax in mixtures with gaseous carbon black. In the case of altax, the zinc oxide speeds up the structuralizing process both in filled and non-filled mixtures. The zinc oxide increases the ratio of the thermal decomposition of altax to free radicals. There are 3 figures, 2 tables and 5 Soviet-bloc references.

ASSOCIATIONS: Volzhskiy filial Nauchno-issledovatel'skogo instituta rezinovoy promyshlennosti i Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti (Volga Branch of the Scientific Research Institute of the Rubber Industry and the Scientific Research Institute of the Rubber Industry)

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37177

S/138/62/000/004/004/008
AO51/A126

15.9130

AUTHORS: Kuz'minskiy, A.S.; Zaytseva, V.D.; Lezhnev, N.N.

TITLE: Protection of natural and synthetic rubber from catalytic oxidation under the action of copper and iron ions

PERIODICAL: Kauchuk i rezina, no. 4, 1962, 10 - 14

TEXT: A study was made of the causes for the different effects of ingredients on the catalytic oxidation of NR (smoked sheets) and CKC-30A (SKS-30A) in the presence of iron and copper. It is assumed that metals with changing valencies can speed up both the reaction of initiation as well as that of chain development. The reaction which determines the rate of initiation is the decomposition of hydroperoxide under the effect of metals. The authors discuss the activation of oxygen and the formation of active intermediate compounds of metal ions with oxygen. The possibility of repressing the accelerated oxidation of NR and SKS-30A in xylene solutions and the solid state was investigated by binding the metal ions into catalytically inactive complexes. Certain rubber ingredients served as the addends in the complexes. Obtained data led to the following conclusions: 1) the higher the concentration of the metal ions in the rubber solution, the faster its viscos-

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Protection of natural.....

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ity drops; 2) the catalytic activity of the copper ions with respect to the rubber oxidation is much higher than the catalytic activity of the iron ions; 3) certain ingredients introduced into the rubber mix have the ability, partly or completely, to suppress the catalytic activity of the copper and iron ions. A further study was made of the catalytic oxidation in the rubber solutions in the presence of anti-aging agents containing amino- and hydroxyl groups, of accelerators containing sulfur and an amino- group in the molecule, and of a vulcanizing agent. The following conclusions were drawn: the accelerators of vulcanization (tetramethylthiuramdisulfide, sodium diethyldithiocarbamate) and anti-aging agents (n-oxyphenyl- β -naphthylamine, dinaphthyl-n-phenylendiamine, dioxydiphenylamine), form firm compounds with the metal ions of varying-valency metals, not having any catalytic activity with respect to natural and synthetic rubbers, but characteristic of the metal ions themselves. These compounds most probably have the structure of intercomplex slats. Certain complex compounds, formed by the metal ion of varying valency, and deactivating substances, are strong inhibitors of rubber oxidation. A new method for synthesizing effective inhibitors is recommended. There are 5 figures and 1 table. The reference to the most recent English-language publication reads as follows: 9.A.Martell, M. Calvin, Chem. of the Metal

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Protection of natural.....

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Chelat Compound (1952).

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti i
Nauchno-issledovatel'skiy institut rezinovykh i lateksnykh izdeliy.
(Scientific Research Institute of the Rubber Industry and Scientific
Research Institute of Rubber and Latex Articles)

4

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S/138/62/000/006/004/008
A051/A126

AUTHORS: Kuz'minskiy, A.S., Ruzer, L.S.

TITLE: Evaluation of scattered radiation deposits when irradiating rubber in press-forms

PERIODICAL: Kauchuk i rezina, no. 6, 1962, 12 - 14

TEXT: Experimental estimations were made of the scattered radiation deposits from the rear and front walls of a press-form, to the absorbed dose of irradiated rubber mixes. The relation between the dose accumulation factor, the thickness of the press-form wall and the article is demonstrated and various parameters are calculated. It was established by the experiments that the irradiation effect of the article is determined by the absorbed dose. This absorbed dose was estimated by the number of transverse bonds formed by radiation. In the method suggested for deposit evaluation, the latter is particularly noticeable when the steel press-form is 1 cm thick or more. It is particularly stressed that serious errors may be introduced in estimating the absorbed dose, if the scattered radiation is not taken into account. It was seen that the accumulation factor for the press-form

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found experimentally is higher by not more than 30% than that calculated for the point source. There are 3 figures.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti
(Scientific Research Institute of the Rubber Industry)

Card 2/2

ANGERT, L.G.; ZENCHENKO, A.I.; KUZ'MINSKIY, A.S.

Structure of butadiene-methylvinylpyridine crude rubber
and of vulcanized rubbers based on it. Kauch.i rez. 21
no.9:5-8 S '62. (MIRA 15:11)

1. Nauchno-issledovatel'skiy institut rezinovoy
promyshlennosti.

(Butadiene) (Rubber, Synthetic) (Pyridine)

S/138/62/000/010/004/008
A051/A126

AUTHORS: Frenkel', R.Sh., Kuz'minskiy, A.S., Morozova, G.M., Gorbunova, V.I.

TITLE: Investigation of the effect of zinc compounds on rubber vulcanization

PERIODICAL: Kauchuk i rezina, no. 10, 1962, 32 - 36

TEXT: An investigation was conducted to determine the action mechanism of zinc oxide and the possibility of producing more effective vulcanization activators. One of the functions of zinc oxide as an activator of vulcanization is its catalytic effect on the decomposition of polysulfide bonds of the vulcanizate. Zinc hydroxide is recommended as a new vulcanization activator, the former reducing the time needed to achieve optimum vulcanization by 2 to 3 times. This new activator also reduces the tendency to scorching; the physico-mechanical properties of the mix are not significantly changed. Best results are obtained with zinc hydroxide combined with ammonium benzoate. Zinc carbonate, as a vulcanization activator, was found to increase the thermal aging resistance of the vulcanizates. The tendency to scorching, as well as the physico-mechanical

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and fatigue properties, remain unchanged. Since zinc oxide, zinc hydroxide, and zinc carbonate have the same specific surface and particle size, the elevated activity of the investigated substances as compared to that of zinc oxide, is explained by the fact that the zinc oxide, formed in their decomposition during the vulcanization process, is more effective than its commercial counterpart. There are 3 figures and 4 tables.

ASSOCIATION: Volzhskiy filial nauchno-issledovatel'skogo instituta rezinovoy promyshlennosti (Volga Branch of the Scientific Research Institute of the Rubber Industry) ✓

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KUZ'MINSKIY, A.S.

Symposium on radiochemistry. Kauch.i rez. 21 no.12:51-53 D. '62.

(MIRA 16:1)

(Hungary—Congresses)

(Rubber research)

KIRPICHNIKOV, P.A.; KUZ'MINSKIY, A.S.; POPOVA, L.M.; SPIRIDONOVA, V.N.

Alkyl aryl esters of pyrocatecholphosphorous acid, new stabilizers
of polymers. Report No.1: Synthesis of alkyl aryl esters of
pyrocatecholphosphorous acid. Trudy KKHTI no.30:47-51 '62.
(MIRA 16:10)

L1337

S/020/62/146/003/013/019
B101/B144

5.4600

AUTHORS: Kuz'minskiy, A. S., Neyman, M. B., Fedoseyeva, T. S.,
Lebedev, Ya. S., Buchachenko, A. L., Chertkova, V. P.

TITLE: Conversions of free radicals in gamma-irradiated polyisoprenes

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 146, no. 3, 1962, 611-614

TEXT: The initial stage of cis- and trans-polyisoprene structuration caused by 10-50 Mrad Co⁶⁰ irradiation was studied. The appearance and disappearance of free radicals was ascertained by recording the epr spectrum. An epr spectrum with a signal width of 14 oersteds was observed on trans-polyisoprene after irradiation at room temperature in vacuo. The structure of the radical causing this signal could not be clarified; probably it was formed by separation of a hydrogen atom from the α -methylene group. At -196°C, irradiated trans-polyisoprene showed a broad singlet due to superposition of various radical spectra. If air was admitted to the ampoule at room temperature, the spectrum passed over into a peroxide spectrum. No epr spectrum appeared in cis-poly-

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Conversions of free radicals ...

isoprene at room temperature, owing to quick radical recombination. At -196°C , cis-polyisoprene showed a spectrum similar to that of trans-compound. The concentration of free radicals at -196°C was higher than at room temperature. The kinetics of disappearance of free radicals is described by an equation of second degree and corresponds to the recombination $\text{R}^{\cdot} + \text{R}^{\cdot} \rightarrow \text{stable product}$. As the slope of the straight lines representing the "reciprocal concentration of free radicals versus time" depends on the dose, it is concluded that in the case of high doses the recombination is impeded by steric hindrances in the amorphous part of the polymer. The following effective constants of radical disappearance have been calculated:

Dose, $\text{r} \cdot 10^{-6}$	10	20	37	47
$\text{K}_{\text{eff}}, \text{sec}^{-1} \cdot 10^4$	6.25	4.33	3.34	2.74

Calculation of the degree of cross linking according to P. L. Flory (J. Chem. Phys., 11, 521 (1943)) showed that at 10 Mrad about 600 isoprene units were between two cross links, that the number of cross links increased with the dose, and that at 150 Mrad 1.2 isoprene units were between two cross links. The steady decrease of K with increasing

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Conversions of free radicals ...

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number of cross links also proves that with increasing density of the network the mobility of molecular chains is impeded and the recombination of free radicals is rendered difficult. There are 4 figures.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti (Scientific Research Institute of the Rubber Industry). Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

PRESENTED: May 21, 1962, by V. N. Kondrat'yev, Academician

SUBMITTED: May 25, 1962

Card 3/3

KUZMINSKIY, A.S., FEDOSEYEVA, T.S., AND CHERTKOVA, V.F.

"The role of free readicals in the radiation vulcanizing of elastomers."

Report submitted to the Conference on ~~Large~~ the Application of Large Radiation
Sources in Industry, Salzburg, Austria 27-31 May 1963

S/138/63/000/003/003/008
A051/A126

AUTHORS: Frenkel', R. Sh., Kuz'minskiy, A. S.

TITLE: The effect of various salts of diphenylguanidine (DPhG) on the rate of vulcanization and the resistance to scorching of rubber mixes based on natural rubber (NR), CKC-30 (SKS-30), and CKE -30 (SKB-30)

PERIODICAL: Kauchuk i rezina, no. 3, 1963, 8 - 9

TEXT: A study was made of the effects of acetic and hydrochloric acid salts of DPhG on the rate of vulcanization and resistance to scorching of rubber mixes based on NR, SKS-30 and SKB-30. Experimental data showed that a replacement of DPhG by its acetic-acid salt has very little effect on the vulcanization rate of the NR-base mixes, while a replacement by its hydrochloric salt sharply impedes the process rate. Experiments with various mixes using only the acetic-acid DPhG as a replacement, showed that rubber mixes containing the acetic-acid DPhG were far more resistant to scorching than similar mixes containing the DPhG. It is concluded that the acetic-acid salt of the DPhG, in combination

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The effect of various salts of...

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with other accelerators, ensures a vulcanization rate of rubber mixes based on NR, SKS-30 and SKB-30 equal to that of DPhG; and a much higher resistance of the mixes to scorching. There are 2 tables and 1 figure.

ASSOCIATION: Volzhskiy filial nauchno-issledovatel'skogo instituta rezinovy promyshlennosti (The Volga Branch of the Scientific Research Institute of the Rubber Industry)

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E 13662-63 EWP(j)/EPF(c)/ENT(m)/BDS AFFTC/ASD Pc-4/Pr-4 RM/WW
 ACCESSION NR: AP3001428 8/0138/63/000/004/0017/0020 67

AUTHOR: Lyubchanskaya, L. I.; Degteva, T. G.; Angert, L. G.; Kuz'minskiy, A. S.

TITLE: Accelerated method for determining the guaranteed storage life span of vulcanized rubbers

SOURCE: Kauchuk i rezina, no. 4, 1963, 17-20

TOPIC TAGS: vulcanized rubber, storage life, creep, stress, relaxation, thermal aging, extension

ABSTRACT: The principle of the method proposed by the authors consists in extrapolating the recorded aging rate of rubbers at high temperatures to fit the thermal conditions of the storage place. To this end it was important not only to select tests sensitive to changes associated with the aging of rubber but also to make sure that the said changes were proceeding at an even rate. Depending on the actual conditions of storage, the thermal accelerated aging test must be conducted on rubbers either under stress or without it, and in the medium the rubber is surrounded with. It is suggested that the thermal tests be conducted in series at 20C intervals, with an upper temperature level of 90-100C for natural rubber for natural rubber and 110-130C for synthetic rubber. In the present investigation stress was chosen as an index of aging. It was conducted on 10x10-mm plugs of vulcanized SKN-18 rubber

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under longitudinal pressure stress in an oil medium at 50, 70, 90, and 110C. The magnitude of the stress, sigma, was measured initially and after various time intervals. From these, the kinetics of continuous relaxation of stress as well as the storage life span of rubber SKN-18 at 25C were calculated, the latter amounting to nine years, which approximates the figure found from practice. Orig. art. has: 9 formulas and 3 charts.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti (Scientific Research Institute of Rubber Industry)

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L 11538-63 EPR/EWP(j)/EPF(c)/EWT(m)/BDS AFFTC/ASD Pa-l/Pe-l/Pr-l RM/WW
 ACCESSION NR: AP3003288 S/0138/63/000/006/0013/0017 72
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AUTHOR: Angert, L. G.; Andreyeva, A. I.; Kuz'minskiy, A. S.

TITLE: Aging of vulcanized rubbers derived from methylvinylpyridine rubber
 under static compression 15

SOURCE: Kauchuk i rezina, no. 6, 1963, 13-17

TOPIC TAGS: compression, static compression, aging of rubber, modulus of
 compression, kinetics of relaxation, thiuram resins, deformation

ABSTRACT: The present study was undertaken to test the aging of vulcanized
 rubber articles subject to pressure in hydraulic installations. Six vulcanized
 rubbers were prepared on a 89% butadiene- and 1% 2-methyl-5-vinylpyridine base.
 Cylinders (8 by 10mm) were squeezed in a vise at a constant 30% deformation and
 allowed to age in the air and in nitrogen for a period of 10-20 days, at tempera-
 tures ranging from 100-150C. The modulus of initial stress of the vulcanized
 rubbers and the magnitude of their residual deformation were determined. It
 was found that the rubbers vulcanized with thiuram as well as with tetrachlor-
 quinone were the most resistant to aging. Unlike the usually observed relation-
 ship between the rates of chemical relaxation and the accumulation of residual

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deformation in rubbers vulcanized with thiuram, sulfur, Altax, and tetraquinone, the present study showed the accumulation of residual deformation proceeding faster than the relaxation of stress. This may be due to the predominance under these conditions of structuration processes. The effect on aging of several organic antioxidants was also studied. Of these p-oxiphenyl-beta-naphthylamine was found to be the most effective in rubber vulcanized with sulfur and Altax. : Orig. art. has: 4 charts and 2 tables.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promy*shlennosti
(Scientific Research Institute of the Rubber Industry)

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EPR/ENP(j)/EPF(c)/EWT(m)/BDS

AFFTC/ASD

Ps-4/Pc-4/Pr-4

RM/WW/AR

S/0138/63/000/C07/0052/0053

ACCESSION NR: AP3004261

AUTHOR: Kuz'minskiy, A. S.

TITLE: Conference of the Council of Economic Cooperation on the aging and stabilization of vulcanized and nonvulcanized rubbers

SOURCE: Kauchuk i rezina, no. 7, 1963, 52-53

TOPIC TAGS: nonvulcanized rubber, vulcanized rubber, aging, stabilizer, oxidation, ozone

ABSTRACT: The conference was held at Poznan, Poland, from Nov. 27 - Dec. 2, 1962 and had 12 topics pertaining to aging and stabilization of rubber on the agenda. The participants were specialists from Bulgaria, Hungary, German Democratic Republic, Poland, Rumania, SSSR, and Czechoslovakia. The leading subjects dealt with the proper selection of raw material, with emphasis on resistance to aging in tropical climate, with performance analysis of rubber items and the role played by aging. In the review papers by Russian and Polish delegates the main attention was centered on the role of mechanical stresses on the temperature aging of rubbers, on aging at high temperatures and in tropical climates, as well as aging under the effect of ionizing radiation. A Soviet woman delegate pointed out methods of

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ACCESSION NR: AP3004261

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synthesis of antifatigue substances. Other Soviet specialists recommended for protection against ozone cracking and for enhancing resistance to fatigue the use of microcrystalline waxes 401CNA, Santoflex, and Antilux. Of great practical importance was the work dealing with aging under stress. The formation of complexes with metals of variable valence was of interest. The Conference pointed out the important work conducted in the USSR, which devotes much attention to the stabilization of vulcanization centers as well as to the stabilization of the molecular chains. Much attention was given to the synthesis of new aging-resistant rubbers. It was pointed out that Esso is producing copolymers of isobutylene, cyclopentadiene, and isoprene that are far more ozone-resistant than butyl rubbers. Thus, e.g., a copolymer containing 1% cyclopentadiene and 2% isoprene not only possesses good mechanical properties but is 80 times more ozone-resistant than butyl rubber. The grafting of special compounds, such as halogenated butyl rubber, to ozone-labile natural rubber was also stressed, as was the addition of 30-40% polyvinylchloride into nitrile rubber. It was the general opinion that the best protection against ozone was offered by paraphenylenediamine derivatives, the top performance belonging to a recently synthesized American derivative of paraphenylenediamine. A number of other substances were listed that protected rubber, such as thiourea, diarylamines, etc. An East German delegate recommended the use of phenyl-beta-naphthylamine as well as microcrystalline waxes, such as Antilux. The Czechoslovak delegate reported

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extensive work on rubber aging conducted in various climatic zones (including Nigeria and tropical China) and recommended the use of not less than 5% ZnO, a number of antioxidants, as well as rubbers containing oil and paraffin. The Polish delegate recommended special rubbers and tires for various climatic zones in Hungary, Poland, Rumania, East Germany, and the SSSR. Unification of the techniques for testing the performance of rubbers in the tropics, as well as unification of formulas, was recommended. A temperature-testing chamber for oxidation studies in rubber at temperatures up to 200C was developed in Czechoslovakia, and an ozone chamber with installations to conduct deformation tests was built by Polish technologists. The Conference adopted a resolution to set up three international climatic stations and also organized the work on aging of rubbers to be conducted by member countries of the Council for Economic Cooperation for the 1963-1965 period.

ASSOCIATION: none

SUBMITTED: 00

DATE ACQ: 21Aug63

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NO REF SOV: 000

OTHER: 000

Card 3/3

S/190/63/005/003/015/024
B101/B203

AUTHORS: Degteva, T. G., Sedova, I. M., Kuz'minskiy, A. S.

TITLE: Thermal degradation of the fluorine-containing Kel-F elastomer at temperatures above 300°C. II

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 5, no. 3, 1963, 378-384

TEXT: Continuing the paper published in Vysokomolek. soyed., 3, 671, 1961, the thermal degradation of Kel-F, a tetrafluoro chloro ethylene - vinylidene fluoride copolymer, was studied in vacuo at 340 - 380°C. Results: (1) The effective activation energy of the degradation process is 53 kcal/mole. (2) Products of molecular weight ~490 are mainly formed in the thermal degradation. The effective activation energy during formation of these products is also 53 kcal/mole. (3) Besides these "high-molecular" products, 8-10% of a low-molecular liquid is formed. The activation energy of its formation is 35 kcal/mole. (4) HCl, HF, and F₂ are formed as gaseous products. (5) The presence of glass accelerates the liberation of the hydrogen halides. (6) A radical-ionic mechanism is assumed for the process

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Thermal degradation of the...

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of degradation. There are 8 figures.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti
(Scientific Research Institute of the Rubber Industry)

SUBMITTED: August 21, 1961

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